Journal of Science and Technology in The Tropics (2015) 11 (1): 1-8

Characteristics of Struvite Precipitate from Palm Oil Mill Effluent

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Received: 15.01.2015; Accepted: 20.02.2015

Abstract Palm oil mill effluent (POME), a residual liquid waste obtained after extraction of oil from the fruits of oil palm is considered one of the main source of contamination of watercourse in Malaysia. POME contained significant amount of nutrients, organic matter and total suspended solids. Recovery of nutrients from POME would be beneficial for agricultural purposes. In this study, to recover nutrient from POME, a lab-scale study was performed to investigate the efficiency of struvite precipitation method. Struvite precipitation was conducted on raw POME using $MgCl_2.6H2O$ + $Na_2HPO_4.12H_2O$ at pH 8. At the end of the test, the water content, mineral and chemical compositions of the precipitate obtained were investigated. In addition, the fertility of the precipitate was evaluated by a set of pot trial tests using Scindapsus Aureus. Test results indicated that, after precipitation test, 92.2% ammonium nitrogen and 100% phosphorus were recovered. X-ray diffraction (XRD) and X-ray fluorescent (XRF) analyses indicated that, after purification, the precipitate is similar to that of struvite. The purified precipitate extracted in this study was found to have a water content of 2799%. Based on the fertility tests, it was found out that the growth of Scindapsus Aureus using struvite precipitate obtained from this study was greater compared to the growth using commercially available fertilizer.

Keywords POME - palm oil - nutrient - struvite - magnesium ammonium phosphate (MAP).

INTRODUCTION

Palm oil industry is regarded as one of the main high impact economic areas in Malaysia. To date, Malaysia is known as the second largest producer of palm oil mill after Indonesia with the production of 39 % of world palm oil production and 44% of world exports [1]. Coupled with this high production, significant quantities of waste are produced in the palm oil mill industry. Amongst other wastes generated, palm oil mill effluent (POME) was identified as one of the main sources of water pollution [2]. POME, when fresh, is a thick brownish colloidal mixture of water, oil and fine suspended solids [3]. Fresh POME is usually discharged at temperature between 80°C - 90°C and contain very high biochemical oxygen demand (BOD) and chemical oxygen demand (COD)[4][5]. POME is also acidic with an average pH of around 4 [6].

Raw POME or partially treated POME is still being discharged into nearby rivers or land, as this is the easiest and cheapest option for disposal [2]. However, due to strict regulatory discharge limits and increasing environmental awareness, POME is now treated prior to being discharge into the environment. Conventional treatment such as ponding system, open tank digester and extended aeration, or closed anaerobic digester and land application systems are the most common and viable treatment techniques adopted [1][7]. In recent years however, a great deal of research and development has been devoted to incorporate advance wastewater treatment technologies for treatment of POME. These treatment techniques include the use of electrocoagulation and biogas recovery technologies [7]. Although these treatments appear to be satisfying the regulatory discharge standards, interestingly, none of these technologies make use of the precious nutrients contained within POME.

Apart from water, oil and suspended solids, POME also contained appreciable amount of nutrients in the form of ammonium-nitrogen (NH4-N), phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) [8]. These elements are vital elements for plant growth. Direct use of POME as fertilizer's substitute is not possible as POME is very concentrated and can be toxic to plants. Alternatively, POME is mixed with empty fruit bunches (EFBs) and other additives and converted into compost. In some cases, vermicomposting technique is also applied [8]. A minimum period of six months is usually required to attain reasonably good quality compost. Hence, this process is somewhat lengthy and cumbersome.

Struvite is a natural occurring soft and unstable mineral, relatively abundant in some soils and modern lakes [9]. It is formed when the combined concentrations of Mg^{2+}, NH_4^+ and $PO_4^{\ 3-}$ exceed its solubility limit at a pH value of 7 to 10.5 [10]. Recovery of nutrient from wastewater via struvite precipitation method have been successfully been achieved both experimentally and theoretically by several researchers in the past [10][11][12]. Struvite crystals have displayed excellent fertilizer qualities under specific conditions when compared to commercially available fertilizers [13]. Qualities such as low solubility, low heavy metal content and rich in nitrogen and phosphorus makes struvite suitable to be used as fertilizer or as fertilizer additives [14][15]. To the author's knowledge recovery of struvite from POME and its characteristics has not yet been explored elsewhere in the literature. This paper, therefore, aims to provide a useful assessment of this technique within this context. The objectives of this study is divided into two parts i) to evaluate the applicability and characteristic of struvite recovered from POME and ii) the fertility of the precipitate is examined and compared with commercially available fertilizer.

MATERIALS AND METHODS

Raw POME samples were collected from a palm oil mill in Jabor, Terengganu. A total number of 3 samples were taken, at 6 monthly intervals. The raw samples were carefully characterized following standard laboratory procedures prior to the experiment. All experiments were conducted under controlled laboratory conditions at 25°C.

The experiments of struvite precipitation were carried out in 500-ml beakers in a batch mode with the following experimental procedure suggested by [10]. Struvite precipitation tests were conducted in 500 ml beaker. The POME sample was then poured into the beakers. Initially, ammonium solution was added to each POME samples to fix the molar ratio of $NH_4^{+/}PO_4^{3-}$ to 4.7 [12]. Excess NH_4^+ is essential to the reaction of struvite crystallization [12]. Once the ratio is fixed, $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ were then added at stoichiometric ratio [10] at pH 8. Note that $MgCl_2.6H_2O$ is added first following $Na_2HPO_4.12H_2O$. The principal chemical reaction for the struvite precipitation is shown in Eq. (1).

$$\begin{aligned} &MgCl_2.6H_2O + Na_2HPO_4.12H_2O + NH_4^+ \\ &\rightarrow MgNH_4PO_4.6H_2O \downarrow + 2NaCl \end{aligned} \quad (1)$$

The mixtures were stirred using a magnetic stirrer for 15 minutes. The pH values of the mixtures were constantly monitored throughout. A Mettler Toledo pH meter was used in this study. After the stirring process, the mixture was allowed to settle for another 15 minutes. Sodium hydroxide solution of 10M was used to increase the pH values of the mixtures and maintained at a constant pH of 8 as suggested by [16]. A much higher pH (i.e. ≤ 8.5), would affect the formation of struvite crystals by the formation of Ca^{2+} impurities. At the end of the tests, the supernatant was collected and characterised. Although the main intention of this study is to evaluate the characteristics of the struvite obtained, however, the improvement in water quality was also assessed. Additional parameters namely, COD, BOD, NH_4^+, PO_4^{3-} and turbidity before and after the tests were measured to evaluate the effectiveness of the technique in improving water quality of treated POME. Duplicate tests were conducted three times to check the reproducibility and reliability of the data.

Purification of struvite precipitate

The struvite precipitate was purified following the methods proposed by Celen and Türker [17] to remove the presence of any impurities. Struvite precipitate was initially dissolved in 1 M of H_2SO_4 solution and inserted in 50 ml centrifuge tubes. The mixtures were then centrifugated at 1000 rpm for 30 minutes. After the centrifugation process, the solutions were filtered. Finally, 1 M of NaOH was used to again increase the pH of the solution to form purified crystals. The purified struvite precipitate was then collected and characterised.

Characteristics of struvite precipitate

The physical properties of purified struvite obtained were determined. In this study, the water content and specific gravity were determined following the methods described in [18]. In addition, the mineralogical and chemical properties of the struvite precipitate were measured using Rigaku Miniflex II X-ray diffraction and Bruker 88-tiger X-ray fluorescence, respectively.

Pot trial tests

In order to evaluate the fertility of the struvite precipitate obtained, series of pot trial tests were conducted. A rapid growing *Scindapsus Aureus* decorative plant was considered for this purpose. The tests were conducted by culturing 3 plants of similar initial conditions (i.e. having similar age and height) in 500 ml beakers using hydroponic approach [18]. Deionised water was filled approximately 150 ml in each beaker before carefully placing each plants in the beakers. This is sufficient to inundate the plants' roots. Each of the plants was grown in three different conditions, (i) deionised water (i.e. control specimen), (ii) deionised water mixed with struvite precipitate and (iii) deionised water mixed with commercially available nitrogen-phosphorus fertilizer. Note that based on the manufacturers' specifications, the usage of commercial fertilizers, are commonly based on the quantity. Due to this fact, approximately 5 g of both struvite and commercial fertilizer were used for direct comparison. This step was taken to imitate practical usage of fertilizer in term of quantity rather than the concentrations of nitrogen-phosphorus contained within. The height and growth of new leaves were continuously monitored until a period of 15 days.

RESULTS AND DISCUSSION

The POME sample collected from Jabor was found to be peaty brown in colour. The characteristics of raw POME used in this study are shown in Table 1.

Table 1. Characteristics of raw POME

Parameters	Values
BOD_5	34,400 - 34,500
COD	50,000 - 89,000
NH_4-N	140 - 180
PO_4^{3-}	190 - 210
Turbidity	418 - 430

Note: all values are in mg/l except for turbidity in NTU

It was noted that the raw POME in this study has low BOD_5/COD ratio due to very high concentration of COD. The NH_4-N concentration was found to be similar to that of PO_4^{3-}.The reduction in concentrations of nutrients and water quality parameters is presented in Table 2. It was noted that removal of NH_4-N was very effective (i.e. 92.20% after adjustment with ammonium solution). Similarly, all other parameters were found to have reduced up to 76.28%, 79.13%, and 91.57% for turbidity, BOD_5 and COD, respectively.

Table 2. Characteristics of POME after struvite precipitation method

Parameters	Values	Average percentage removal (%)
BOD_5	7,200	79.13
COD	7,500	91.57
NH_4-N	26	92.20
PO_4^{3-}	-	100
Turbidity	102	76.28

Note: all values are in mg/l except for turbidity in NTU

Test results indicated that, not only struvite was obtained, improvements in the water quality parameters were also observed. Comparisons with allowable limits for effluent discharge however indicated that further treatment is required to further improve the quality of POME after precipitation of struvite. Similar observation was made by Li and Zhao [10], struvite precipitation method can only be used as pretreatment as other water quality parameters are still greater than allowable discharge limits.

Characteristics of struvite precipitate

Commonly, pure struvite as $MgNH_4PO_4.6H_2O$ is a white crystalline powder. Other struvite precipitate such as brown to yellowish has also been observed from landfill leachate [10]. However, in this study, the struvite precipitate generated from the POME samples was dark brown in colour. Comparison between struvite obtained directly after precipitate and after purification is presented in Fig. 1.

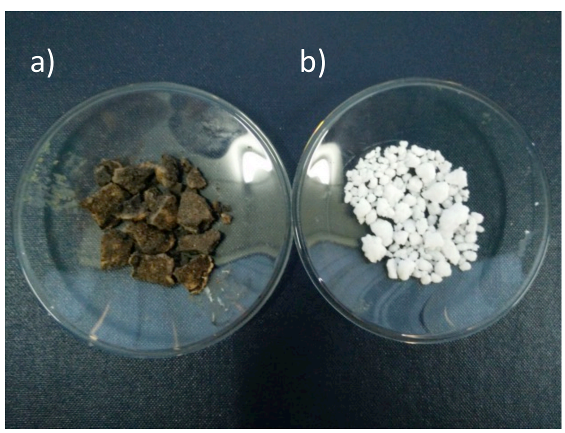

Figure 1. Comparison of struvite (a) before purification, (b) after purification

This colouration of precipitate is anticipated may have originated from co-precipitation with peaty brown organic suspended solids in the raw POME. The precipitate is also found to be very wet and contained significant amount of water. After purification however, the colour of the struvite precipitate was found to change from dark brown to white. Qualitatively, it is anticipated that pure struvite crystals were formed. This finding is supported by both XRD and XRF analyses. Table 2 summarizes the characteristics of struvite precipitate after purification process. Based on Fig. 1, it was noted that the precipitate consist of only struvite minerals.

Table 2. Characteristics of struvite precipitate from POME

Parameters	Values
Specific gravity, Gs	1.72
Water content (%)	2799
Mineral composition (%)	
Struvite	100
Chemical composition (%)	
Magnesium	9.83
Phosphorus	12.47
Hydrogen	6.57
Nitrogen	5.71
Oxygen	58.85

Figure 2 shows the XRD analysis of struvite precipitate obtained in this study. No traces of impurities or toxic elements were found after the completion of the purification process. The water content of the precipitate was found to be very high (i.e. 2799%) indicating that the mass of precipitate contained more water than actual struvite crystal. Struvite precipitates, commonly in hydrated form are usually dried at 60 °C to minimize water loss [19]. From practical point of view however, removing excess water is necessary for packaging, transporting and storage of struvite as fertilizers. Drying of the precipitate reduces the total mass to about 2799% of its original mass. This in turn would reduce cost for transportation and handling of struvite.

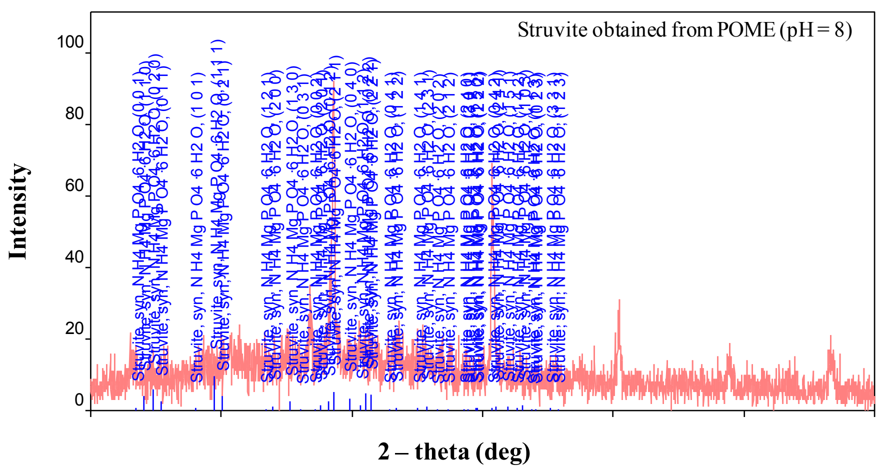

Figure 2. Xray-diffraction analysis of struvite obtained from POME at pH = 8

Fertility of struvite precipitate

Figures 3 and 4 show the image of pot trial tests conducted in this study using *Scindapsus Aureus* and length of leaves with elapsed time. It was found out that 5 days is sufficient for the plants to sprout new set of leaves. The height of the plants remained somewhat unchanged throughout the testing period. It was noted that, at the end of the test, only 2 new leaves was observed. Interestingly, the plant cultured in struvite was found to have grown 8 new leaves, whereas only 4 new leaves were observed for plant cultured using commercialized fertilizer. Towards the end of the study, some yellowing and curling of leaves were observed for plant cultured in deionised water, indicating deficiency in nutrient (see Fig.3a) [20].

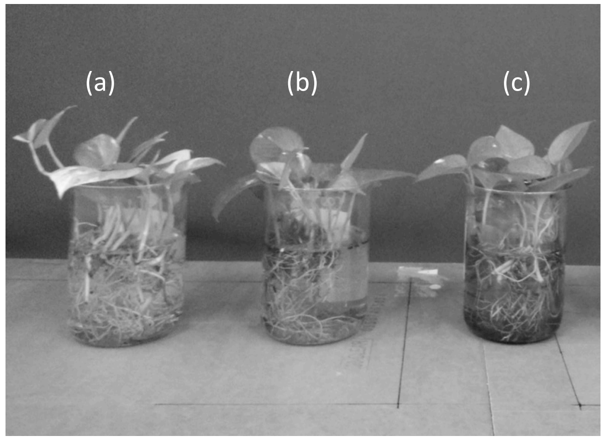

Figure 3. Pot trial test for *Scindapsus Aureus* (a) control, (b) commercial fertilizer and (c) struvite from POME

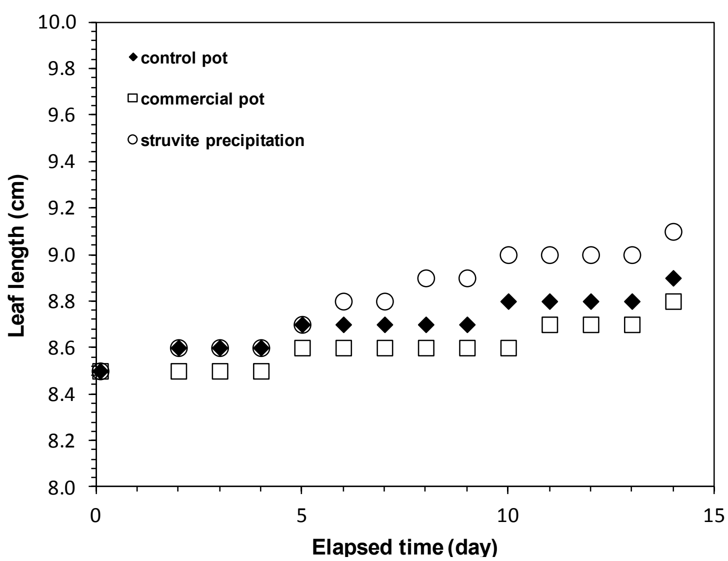

Figure 4. Length of leaf with elapsed time

It should be highlighted that even though the compositions of struvite is lacking some other essential nutrients (i.e. potassium) commonly found in fertile soil and commercially available fertilizers [20], the use of struvite as fertilizer or fertilizer additives was found to be sufficient for culturing *Scindapsus Aureus* in this study up to a period of 15 days. Similar observation was also made by [10][21] using different plant species. Although the test was conducted in a short period of time, the superiority of struvite precipitate was successfully evaluated.

CONCLUSION

An investigation has been made on struvite precipitation of POME. The following conclusion can be made:

- Struvite precipitation method can be used to extract struvite from raw POME using $MgCl_2 \cdot 6H_2O$ + $Na_2HPO_4 \cdot 12H_2O$ at pH 8.

- Pure struvite can be obtained by simple purification process using acid solution and centrifugation technique by removing unwanted impurities.
- Struvite precipitate obtained using struvite precipitation was found to contained significant amount of water. Excess water should be drained or dried to reduce the total mass of struvite precipitate.
- Water quality of raw POME can be improved, however further treatment are required to fulfil strict regulatory discharge limits.

Acknowledgement - The authors would gratefully like to acknowledge the financial support provided by Ministry of Higher Education of Malaysia for sponsoring the research project under RAGS grant RDU 131417.

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